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Novel Fluoroalkene−Methyl Acrylate Copolymers by Atom Transfer Radical Polymerization

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Introduction

Fluoropolymers and their copolymers with functional comonomers are interesting materials. The incorporation of fluorine-containing moieties in polymers results in materials with high thermal and chemical resistance and oil- and water-repellant surfaces.[1,2] Fluoropolymer thin films also possess low permittivity, low dielectric constants, low flammability, excellent chemical inertness, low refractive index, and low-loss optical wave guiding: properties that are desirable for electronic and optoelectronic applications.[3] Furthermore, the specific surface properties can be altered depending upon the amount and type of fluorinated segments present. Arnold et al. have synthesized fluorinated side chain acrylate polymers and its block copolymers with styrene employing azobis(isobutyronitrile) (AIBN) as an initiator in supercritical carbon dioxide. These materials show higher gas permeabilities and lower selectivities than the corresponding methyl acrylate derivatives.[4] A particularly interesting class of hitherto unknown fluorine containing polymers are those derived from the controlled copolymerization of fluoroalkenes with simple acrylates. The acrylate moieties should provide good adhesion to a wide range of substrates whereas the segregation of the fluoroalkyl side chains toward the air side of the films should lead to low surface energy hydrophobic surfaces.

Recently we[5,6] and others[7] have demonstrated that acrylates can be radically copolymerized with 1-alkenes in a controlled fashion, e.g., by atom transfer radical polymerization (ATRP). In the case of styrene, the ATRP of the fluorinated derivatives have been shown to proceed faster than that of the parent monomer.[8] This paper reports the first random copolymerization of methyl acrylate with fluorinated alkenes ($R_fCH{=}CH_2$) employing the ATRP protocol. As with styrene, perfluorination of the pendant alkyl group increases monomer reactivity. The resulting copolymers are hydrophobic in nature with a water contact angle as high as 118° on spin-coated surfaces. Furthermore, the unique block terpolymer, poly[(MA-*co*-ethene)-*b*-(MA-*co*-nonafluorohexene)], was also synthesized by sequential addition of ethene and nonafluoro-1-hexene to an acrylate copolymerization system.

Experimental Section

Methyl acrylate (MA, 99%) (Aldrich) was passed through a column to remove the inhibitor and distilled over CaH_2 before polymerization. Ethyl-2-bromopropionate (99%), Cu(I)Br (99.99%), pentamethyldiethylenetriamine (PMDETA) (99%), and azobis(isobutyronitrile) (AIBN, 98%) (all from Aldrich) were used as received. 3,3,4,4,5,5,6,6,6-Nonafluoro-1-hexene (F-hexene) (99%), 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octene (F-octene) (99%), and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decene (F-decene) (99%) (Aldrich) were degassed by three freeze−pump−thaw cycles and stored over molecular sieves in the glovebox. Molecular weights of the polymers were determined by size exclusion chromatography (SEC) using a Shimadzu instrument equipped with a series of three Styragel columns (Styragel HR 7.8 × 300 mm columns with 5 μm bead size: 100−10 000, 500−30 000, and 5000−6 000 000 Da) from Polymer Laboratory, and a RI as well as a UV detector (254 nm). Measurements were performed in chloroform at 35 °C with a flow rate of 1 mL/min. Molecular weights were calculated employing narrow molecular weight polystyrene standards from Polymer Laboratories. The ^1H (300 and 400 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a Bruker DPX 300 or DRX 400 instrument, and ^{19}F (282.1 MHz) NMR spectra were recorded on Bruker CDPX-300 instrument at room temperature in $CDCl_3$. The chemical shifts are reported in δ ppm with reference to $CHCl_3$ for ^1H and ^{13}C NMR and C_6F_6 for ^{19}F NMR. The chloroform solutions of the polymer were passed through the alumina column, and the polymers were isolated by reprecipitating in hexane. These polymers were redissolved in chloroform and spin-coated on glass slides. The XPS analysis was performed on Kratos instrument with monochromatic Al X-ray source (1486.6 eV) operated at 280 W and a pressure of 10^{-9} Torr. The analysis was carried out using a takeoff angle of 90° with respect to sample plane. The approximate sampling depth for analysis was 50 Å, and the quantification of atomic concentration was performed from relative sensitivity with a linear background. The values reported here are with 2−4% systematic error. The water contact angle on the polymer thin films spin-coated on glass slides with 3−5% w/w solution in $CHCl_3$ was measured with contact angle goniometer with an accuracy of ±3°. The reported values are the average of three measurements at three different positions of the film.

The copolymerization reactions were performed at 90 °C employing ethyl 2-bromopropionate as the initiator and with Cu(I)Br and PMDETA as the catalyst system. The polymerizations were performed in bulk as well as in solution with initiator:Cu(I)Br:PMDETA ratio of 1:1:1. The copolymerization results are listed in Table 1. In a typical copolymerization experiment involving MA and F-hexene, a flask was charged inside a nitrogen-filled glovebox with 5 g (0.058 mol) of MA, 2 g (0.008 mol) of F-hexene, 0.085 g (0.000 47 mol) of ethyl 2-bromopropionate, 0.067 g (0.000 47 mol) of Cu(I)Br, and 0.081 g (0.000 47 mol) of PMDETA. The flask was then immersed in an oil bath preheated at 90 °C. After 16 h the flask was removed from the bath and cooled rapidly down to ambient temperature. The polymer was isolated by precipitation in hexane and dried under vacuum. Yield: 77%. The obtained polymer had M_n of 17 900 and PDI of 1.26 with 6.8 mol % alkene incorporation.

The copolymerization reaction kinetics of MA with three fluoroalkene comonomers F-hexene, F-octene, and F-decene were performed in anisole solution. Samples were withdrawn at different time intervals and analyzed by ^1H NMR spectroscopy and SEC. The overall conversion of the samples withdrawn at different time intervals was calculated from ^1H NMR spectra by comparing the integral area of alkene protons of the starting precursor with the main chain aliphatic protons of the resulting polymer. All three copolymerization reactions showed a linear increase in molecular weight with increase in conversion. The molecular weight distribution (PDI) remained below 1.3.

Results and Discussion

The ATRP copolymerization results are shown in Table 1. The fluoroalkenes ($R_fCH{=}CH_2$) copolymerize

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Table 1. Atom Transfer Radical Copolymerization of Methyl Acrylate with Alkenes[a]

run	MA (g)	1-alkene (g)	MA:1-alkene (molar ratio)	time	yield (%)	SEC[c]		alkene incorp (mol %)[d]
						M_n	PDI	
1	5	1-hexene (2)	70:30	16 h	55	13 800	1.26	4.9
2	5	F-hexene (1)	93:7	16 h	92	18 600	1.28	5.3
3	5	F-hexene (2)	88:12	16 h	77	17 900	1.26	6.8
4	3	F-hexene (3)	74:26	12 h	50	15 300	1.33	12.1
5	0.5	F-hexene (1.4)	50:50	40 min	21	9 200	1.20	9.1
6	0.5	F-hexene (2.8)	33:67	40 min	9	7 500	1.23	11.8
7[b]	1	F-octene (4)	50:50	16 h	21	19 000	1.33	10.4
8	1	F-decene (2)	72:28	70 min	35	10 900	1.20	8.1

[a] Reaction conditions: [MA]:[ethyl 2-bromopropionate], 1:0.008; [ethyl 2-bromopropionate]:[CuBr]:[pentamethyldiethylenetriamine], 1:1:1; 90 °C. [b] Anisole, 1 g. [c] By size exclusion chromatography using polystyrene standards. [d] By ^{1}H NMR spectroscopy. F-hexene: 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene; F-octene: 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octene; F-decene: 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decene; M_n: number-average molecular weight; PDI (polydispersity index): M_w/M_n.

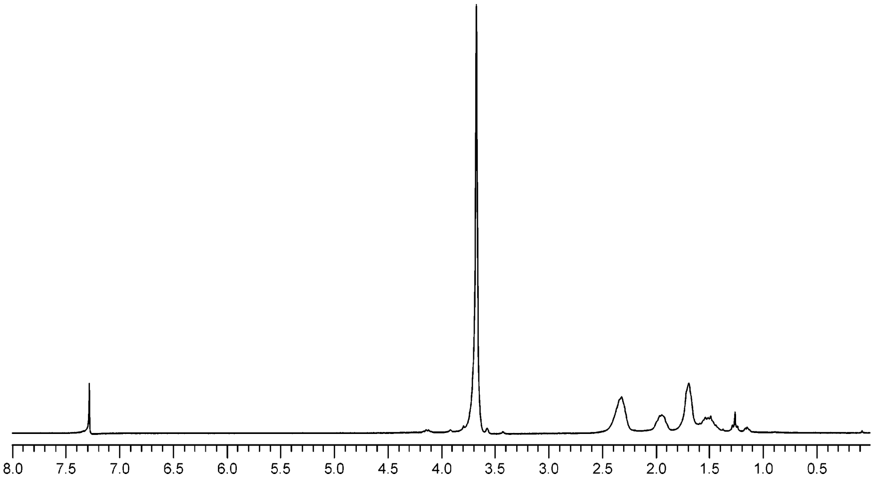

Figure 1. ^{1}H NMR ($CDCl_3$) of poly(MA/F-hexene) copolymer containing 11.8 mol % of F-hexene (3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene).

faster (see below) and proceed with significantly higher incorporation compared to the parent 1-alkene. The polydispersities of the copolymers obtained are relatively low, suggesting controlled polymerizations. The single monomodal peak in SEC with RI and UV detectors clearly suggests that the obtained polymers are copolymers rather than mixtures of two homopolymers. Increasing the relative amount of fluoroalkene in the monomer feed resulted in higher incorporation in the resultant copolymer but a reduced overall yield. The ^{1}H NMR spectra of the copolymers show a methoxy resonance at 3.6 ppm, whereas the main-chain proton resonances from acrylate and fluoroalkene units overlap between 1.2 and 2.4 ppm (Figure 1). The copolymer compositions were determined from the relative integrations of the two sets of resonances. The random nature of obtained copolymers was verified by ^{13}C NMR and gradient ^{1}H−^{13}C HMQC NMR spectroscopy. The CH_2 resonances from MA at 35.4 and 35.8 ppm and CH resonances at 40.3 and 41.6 ppm suggest the formation of MA−F-hexene−MA and MA−MA−MA triads, respectively.[6]

For comparison, the conventional AIBN-initiated radical copolymerizations of MA with the fluorinated 1-alkenes were also performed (Table 2). The overall alkene incorporation in the copolymer was similar to that observed with ATRP. However, as expected, the molecular weight and polydispersity values were significantly higher in the former because of the uncontrolled nature of the copolymerizations.

Figure 2 shows plots of ln[M]$_0$/[M] as a function of time for the homopolymerization of MA as well as copolymerizations of MA with F-decene and 1-decene. The linearity of the plots suggests first-order kinetics, and furthermore, the reaction involving heptadecafluoro-1-decene is significantly faster than with 1-decene, although slower than MA homopolymerization. A similar plot for the copolymerization of MA with F-hexene (not shown) is virtually superimposable with that for MA/F-decene copolymerization, indicating that the length of the perfluoro pendant has little effect on copolymerization rate. For the copolymerization of the MA with the three fluoroalkenes examined, the molecular weight of the obtained copolymer increased with conversion while the polydispersity remained less than 1.2 (for example, Figure 3).

Table 2. Azobis(isobutyronitrile) (AIBN)-Initiated Copolymerization of Methyl Acrylate with Alkenes[a]

run	alkene	time (h)	yield (%)	SEC[c]		alkene incorp (mol %)[d]
				M_n	PDI	
1[b]	1-hexene	21	25	161 000	1.7	11.6
2	F-hexene	23	27	378 300	2.61	12.7
3[b]	1-octene	21	25	115 000	1.6	12.9
4	F-octene	23	25	186 200	2.55	10.8
5	F-decene	23	31	716 700	2.12	15.8

[a] Reaction conditions: MA, 0.5 g (0.0058 mol); MA:fluoroalkene, 1:1; AIBN, 0.003 g (0.000 015 mol); PhCl, 4 mL; 60 °C. [b] Reference 6. [c] By SEC using polystyrene standards. [d] By ^{1}H NMR spectroscopy. F-hexene: 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene; F-octene: 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octene; F-decene: 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decene; M_n: number-average molecular weight; PDI (polydispersity index): M_w/M_n.

The effect of initiator concentration on MA/F-hexene copolymerization was investigated. A 3:1 molar ratio of

Table 3. Effect of Initiator Concentration on the Atom Transfer Radical Copolymerization of Methyl Acrylate with F-Hexene[a]

				SEC[c]		
run	M_n (target)[b]	ethyl 2-bromopropionate (mol)	yield (%)	M_n	PDI	alkene incorp (mol %)[d]
1	5 000	0.000 2	53	6 500	1.20	15.1
2	10 000	0.000 1	48	10 600	1.16	12.5
3	15 000	0.000 07	50	14 800	1.19	12.1
4	20 000	0.000 05	47.5	23 700	1.16	8.9

[a] Reaction conditions: MA, 1 g (0.011 61 mol); F-hexene, 1 g (0.0040 mol); [ethyl 2-bromopropionate]:[CuBr]:[pentamethyldiethylenetriamine], 1:1:1; 90 °C; 1 h. [b] Based on 100% conversion of MA. [c] By SEC using polystyrene standards. [d] By ^{1}H NMR spectroscopy. F-hexene: 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene; M_n: number-average molecular weight; PDI (polydispersity index): M_w/M_n.

Table 4. Surface Property Measurements by XPS and Contact Angle for Methyl Acrylate−Fluoroalkene Copolymers

			SEC			
sample	polymer	alkene (mol %)[a]	M_n	PDI	F/C × 100[b]	CA (deg)[c]
1	poly(MA/F-hexene)	6.8	17 900	1.26	17.3	107.3
2	poly(MA/F-hexene)	9.8	11 600	1.24	25.5	108.0
3	poly(MA/F-hexene)	12.1	15 300	1.33	30.4	110.0
4	poly(MA/F-decene)	6.5	12 100	1.92	57.3	114.7
5	poly(MA/F-decene)	8.1	10 900	1.20	56.5	117.9

[a] By ^{1}H NMR spectroscopy. [b] By XPS. [c] Contact angle with water droplet. F-hexene: 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene; F-decene: 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decene.

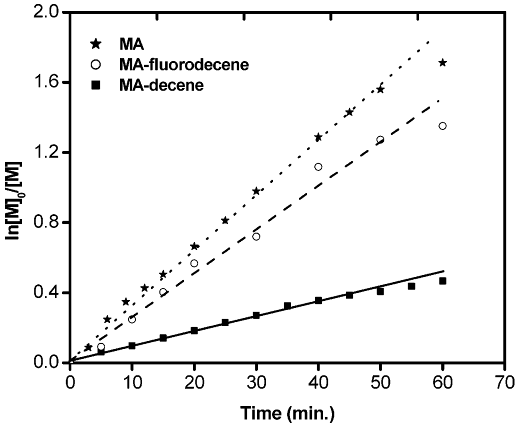

Figure 2. Comparative copolymerization kinetics of MA with F-decene and 1-decene. Reaction conditions: ethyl 2-bromopropionate, 0.000 47 mol; [ethyl 2-bromopropionate]:[CuBr]:[pentamethyldiethylenetriamine], 1:1:1; anisole, 2 g; 90 °C. MA homopolymerization: MA, 0.058 mol; MA/F-decene copolymerization: MA, 0.058 mol; F-decene, 0.0067 mol; MA/1-decene copolymerization: MA, 0.058 mol; 1-decene, 0.0067 mol. F-decene: 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decene.

MA to F-hexene was maintained in the feed and four different M_n values, 5000, 10 000, 15 000 and 20 000, were targeted. As shown in Table 3, the molecular weight of the copolymers increases with decreasing initiator concentration. Moreover, M_n values close to those targeted were obtained, further illustrating the controlled nature of the copolymerizations.

The controlled nature of the copolymerizations was also demonstrated by synthesis of the novel block copolymer, poly[(MA-*co*-ethene)-*b*-(MA-*co*-nonafluorohexene)], by sequential addition of ethene and F-hexene to the MA copolymerization system. In the first step the reactor was charged with MA and ethene. After performing the ATRP copolymerization, the ethene was vented and the flask was flushed with nitrogen. A small part of the reaction mixture was syringed out for determination of molecular weight and copolymer composition. The MA−ethene copolymer withdrawn after the first step had $M_n = 7100$ and $M_w/M_n = 1.10$, with 8.1% ethene incorporation. The flask was then charged with nonafluorohexene, and the polymerization was continued. The final terpolymer had $M_n = 20\ 500$ and $M_w/M_n = 1.43$ (see Figure 4). The polydispersity of the final terpolymer was somewhat high, suggesting that not all the chains formed after the first step participated in the second copolymerization. The incorporation of F-hexene in the final terpolymer was confirmed by ^{19}F NMR spectroscopy which showed the CF_3 resonance at −77.4 ppm and CF_2 resonances between −120 and −125 ppm. However, it was difficult to calculate the F-hexene incorporation by ^{1}H NMR spectroscopy as the main-chain proton resonances of the incorporated F-hexene overlaps with main-chain protons from both MA and ethene units, appearing between 1.2 and 2.4 ppm.

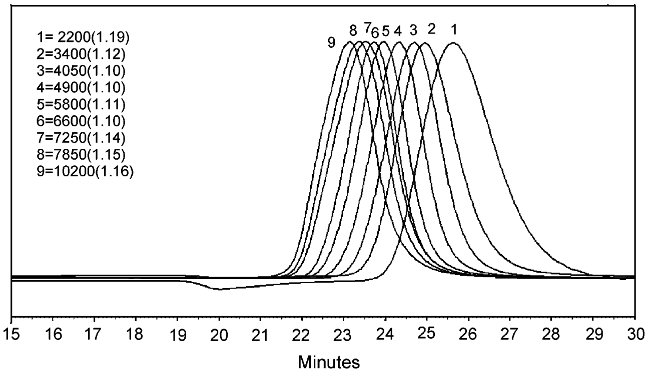

Figure 3. SEC traces of poly(MA/F-hexene) copolymerization with increased conversion. Reaction conditions: MA, 0.058 mol; F-hexene, 0.0067 mol; ethyl 2-bromopropionate, 0.000 47 mol; [ethyl 2-bromopropionate]:[CuBr]:[pentamethyldiethylenetriamine], 1:1:1; anisole, 2 g; 90 °C. F-hexene: 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene.

The surface properties of the copolymers were investigated by X-ray photoelectron spectroscopy (XPS) with a takeoff angle of 90° on polymer thin films spin-coated on glass surfaces. It was observed that the fluorine enrichment at the air-side surface of these copolymers increases with both increase in the length of the perfluoro side chain and the degree of incorporation of the fluoroalkene in the copolymer, and this is mirrored by the increase in water drop contact angle. For example, for poly(MA/F-hexene), the F/C% and the contact angle increase from 17.3 to 30.4 and from 107.3°

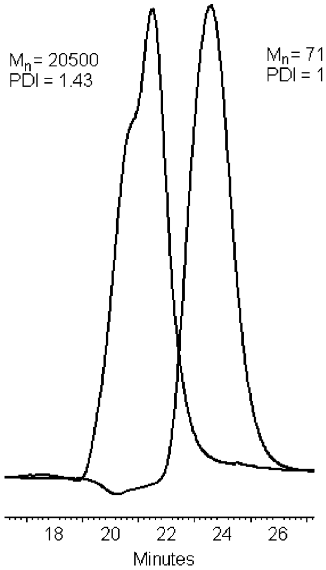

Figure 4. SEC traces of poly(MA-ethene) copolymer and the subsequently formed poly[(MA/ethene)-*b*-(MA/F-hexene)] block terpolymer. Reaction condition for first step: MA, 0.116 mol; ethyl 2-bromopropionate, 0.000 17 mol; [ethyl 2-bromopropionate]:[CuBr]:[pentamethyldiethylenetriamine], 1:1:1; ethene, 700 psi; 1 h; 90 °C. Conditions for second step: F-hexene, 0.020 mol; 6 h; 90 °C. F-hexene: 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene.

to 110.0°, respectively, as the F-hexene content increases from 6.8 to 12.1%. In the same vein, for similar F-alkene incorporation (~6.5 mol %), the F/C% and the contact angle increase from 17.3 to 57.3 and from 107.3° to 114.7°, respectively, on moving from F-hexene to F-decene. These observations suggest the segregation of the fluoroalkyl side chains toward the air side of the films, resulting in low surface energy hydrophobic surfaces. Similar effects have been described previously for polystyrene derivatives.[1]

In conclusion, we have demonstrated the first controlled ATRP of methyl acrylate with fluoralkenes. The copolymerization rate and the extent of alkene incorporation are higher than those observed with simple 1-alkenes. Novel block terpolymers of MA with alkenes and fluoroalkenes can be also synthesized. Both the XPS and contact angle measurements of films reveal that the fluorinated side chains of the copolymers have a tendency to segregate and enrich at the air side, resulting in low surface energy hydrophobic surfaces.

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